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TITLE   MODELING OF IRRADIATION-INDUCED AMORPHIZATION

IN A TITANATE CERAMIC

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MODELING OF IRRADIATION-INDUCED AMORPHIZATION

IN A TITANATE CERAMIC*

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Abstract

Calculations have been carried out to model the alpha
decay-induced conversion of a titanate ceramic ($CaPuTi_2O_7$) from the
crystalline state to an amorphous condition. Experimental results have
shown that the disordered state varies with irradiation temperature and
extent of redamage, and so special consideration is given to those
factors. Results of these calculations are applied to the analysis of
dimensional changes during irradiation at various temperatures and
release of stored energy on recovery to the crystalline state. Modeling
results appear to show that it is possible to convert to the amorphous
state under irradiation by two different processes. Modeling is also
employed to extend experimental results on swelling from the present
data base to a high damage rate characteristic of ion implantation and
the low rates typical of nuclear waste storage and self-damage of
natural mineral analogues.

I. Introduction

Some ceramics can be converted from the crystalline state to an atomically-disordered (i.e., amorphous or metamict) condition by particle irradiation. Studies of synthetic zirconolite ($CaZrTi_2O_7$) and related materials such as the $CaPuTi_2O_7$ investigated here have shown that these titanates become disordered when implanted with Pb ions [1], irradiated with neutrons [2], or subjected to self-damage by doping with short half-life ^{238}Pu [3-5] or ^{244}Cm [6] isotopes. The mineral zirconolite can also be converted to the metamict condition over geologic times by alpha decay of naturally-present U or Th ions [7,8]. In all these cases metamictization results from gradual accumulation of disordered damage tracks formed during irradiation. EXAFS studies of mineral forms [9] show that the principal difference between the crystalline and amorphous structures is the misalignment, in the latter case, of TiO_6 octahedral structural units.

Important factors in the conversion process are damage dose, extent of redamage of a given microvolume, and concurrent recovery processes related to the temperature of irradiation. Recrystallization on heating after irradiation is primarily affected by fraction of material converted to the amorphous condition. At relatively low

temperatures (near 300K)* zirconolite-like ceramics exhibit similar
damage response as a function of dose over twelve orders-of-magnitude in
damage rate [3], indicating that concurrent recovery at this temperature
is minimal. However, the exact process for amorphization of the natural
minerals is not known since the swelling versus dose is not known. We
will show that the final state may be affected by this dose dependence.
Increasing the irradiation temperature of CaPuTi$_2$O$_7$ to 575K has a
significant effect on the conversion process, both in reducing the rate
at which conversion takes place and in causing formation of a
less-disordered metamict state [3,5] for the terminal phase. At 875K
with the damage rate characteristic of alpha decay of ^{239}Pu, recovery
overwhelms damage and the material remains crystalline [3]. This
behavior is shown in Fig. 1, where swelling is plotted against dose.

Details of the evolution of the damage state in metamict-prone
ceramics and its effect on physical properties are poorly understood,
and so it is useful to employ computer modeling to trace that evolution
and establish the basis for predicting materials response at different

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*Irradiation temperatures for samples subjected to Pb ion bombardment,
self-damage from doping with Pu or Cm, or damage from a natural content
of U or Th are not precisely 300K. However, transmission electron
microscopic examinations [1,3,8] have revealed no discernable
differences in damage response.

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damage rates from those for which experimental data exist. In the work reported here damage and redamage effects in $CaPuTi_2O_7$ are modeled. Data on temperature-dependence of damage response is then used to predict behavior at a higher irradiation flux (characteristic of ion implantation) and a lower flux (typical of that to be encountered in permanent storage of nuclear waste and in natural mineral analogues).

II. Model for Amorphization of $CaPuTi_2O_7$

The ultimate goal here is to develop a model that would contain all the experimentally observed features of the process. In particular the model must show no amorphization for self-irradiation at 875 K and complete amorphization at temperatures at and below 575 K. During the course of several investigations, a variety of evidence has accumulated to support the existence of several different metamict states: viz., samples show at least two amorphous states for irradiations at 350 K and these are different from the state or states seen for irradiations at 575 K. The difference in the density for the terminal phases shown in Fig. 1 as well as the maximum in the swelling versus dose curve at 350 K supports these contentions. Additional evidence has been observed in electron diffraction [5] and in recovery of the dilated state on annealing at 875 K[10]. Also the energy released on annealing samples irradiated at 350 K passes through a maximum with dose and levels off at about 51 kJ/kg for high doses[4]. This last result is consistent with a change in the amorphous state from one exhibiting a high stored energy to a distinctly different one characterized by a much lower value.

Amorphization by self-irradiation occurs in this material

through the damage created after the α-decay of the ^{238}Pu. The damage process occurs randomly and can be described using Poisson statistics[11,12]. The fraction of material that has been damaged by n-damage tracks after irradiation for time t is

$$F_n = \frac{(\lambda t)^n}{n!} \exp(-\lambda t), \qquad (1)$$

where λ is the mean cascade rate in the volume and is the product of the damage track volume, V, and the cascade rate per unit volume, N_a. Using this equation we can calculate the fraction of material that is undamaged,

$$F_0 = \exp(-\lambda t), \qquad (2)$$

and the fraction of material that has been damaged by a single damage track,

$$F_1 = \lambda t \exp(-\lambda t). \qquad (3)$$

Using these results we can then find the fraction that has been damaged by 2 or more damage tracks,

$$G_2 = 1 - F_0 - F_1. \qquad (4)$$

A plot of F_0, F_1, G_1, and G_2 versus dose for CaPuTi$_2$O$_7$ is shown in Fig. 2. In the model that follows, the density of a sample will depend on each of these fractions.

In our simplest model we assume that the material initially has

a density of d_o. As damage events occur the damaged volume V will have a new density of d_1, and after re-irradiation the structure of the damaged region will relax to a density d_R. Using the previously defined equations for the various volume fractions, the density as a function of time will be

$$d = d_R + [(d_o - d_R)+(d_1 - d_R) \lambda t] \exp (-\lambda t). \qquad (5)$$

Swelling, S, is defined as the change in volume per unit volume; therefore,

$$S = (d - d_o)/ d. \qquad (6)$$

Figure 3 shows a family of curves that are obtained using a value of $r_1 = d_1/d_o = 0.95$ and a range of $r_m = d_R/d_o$. The general shape varies from curves having a low maximum to those having a long nearly linear dependence on time. Curves showing the maximum occur for $d_1 < d_R$ and the curves with a more linear curve occur for $d_1 \approx d_o$. These observations lead us to attempt to fit the results in Fig. 1.

The model described above was used to calculate time-dependence (i.e., dose-dependence) of damage response in $CaPuTi_nO_7$ near 350 K and 575 K as shown in Fig. 1. The results of these calculations are shown in Fig. 4. Given that the cascade rate per unit volume per unit time, N_o, in these samples is 1.53×10^{11} $\alpha/m^3 \cdot s$, the only adjustable parameters are the volume of each cascade and the ratios in densities, $r_1 = d_1/d_o$ and $r_m = d_R/d_o$. Values of $r_1 = 0.92$ and $r_m = 0.952$ gave the best fit to the 350 K data, while for the 575 K curve the corresponding

values were $r_1 = 0.99$ and $r_m = 0.953$. The fitting process was trial-and-error with care taken to fit the limiting swelling values, the average initial slope of the curves and the position of the maximum in the 350 K curve. The volumes of the cascades were allowed to vary and the final values were 7.19×10^{-24} m^3 and 1.31×10^{-25} m^3 for 350 K and 575 K, respectively. Since no amorphous state was observed at 875 K, no modelling was done for this sample and the predicted swelling curve would lie along the time (i.e. dose) axis. The consequences of these results are discussed in the following sections.

Part of the temperature-dependence of damage response is represented by the different values needed to fit the swelling curves at different temperatures. One method to predict the swelling behavior at temperatures other than 350 K and 575 K would be to extrapolate the present results to those temperatures. However, some of the differences are believed to come from different damage mechanisms operating at various temperatures. Changes in the damage mechanisms depend on the kinetics of recrystallization, relaxation, and the damage structure within the damage track.

Some estimates of the temperature and dose-rate dependence of some of these processes have been made based on other thermal measurements. Weber et al.[6] measured the activation energy Q for recrystallization to be 5.8 eV in ^{244}Cm-doped zirconolite using differential thermal analysis (DTA). The recrystallization peak occurred at 945 K for a thermal scan rate of 5 K/min. It can be shown that the recrystallization process lasted 277 s at this rate. (This time is that required for the temperature scan to cross the width of the peak

at 1/2 height.) If we assume the recrystallization rate is proportional to t^{-1} where t is measured as above, the time for recrystallization can be found at any temperature,

$$t = t_o \exp (Q/kT), \qquad (7)$$

where $t_o = 6.24 \times 10^{-29}$ s. If a further assumption is made that if enough radiation occurred during the time for recrystallization to amorphize the sample, the sample would not recrystallize. The use of an alpha decay dose equivalent to 100 days of self-irradiation in the $CaPuTi_2O_7$, (i.e., well into the process of damage accumulation as shown in Fig. 1) gives an equation describing the recrystallization temperature versus damage rate,

$$T_{ii} = Q/[k \ln(0.173/N_\alpha \ t_o)]. \qquad (8)$$

The constant k is calculated using the equivalence of 1.53×10^{10} $\alpha/m^3 \cdot s$ = 2×10^{-9} dpa/s[3] and N_α in eq(8) is in units of dpa/s.

A second, smaller DTA peak has been seen in heavily irradiated material[4,6] which may be associated with the relaxation of an amorphous condition from that observed at 350 K to that observed at 575 K. If the activation energy for the subsidiary peak determined by Weber et al.[6] of 3.1 eV is assumed and an analysis similar to that above for recrystallization is performed, the temperature for relaxation, T_{ii}, is found in an equation equivalent to eq(8) with a value of $t_{ii} = 8.46 \times 10^{-30}$ s. The relaxation temperature for 2×10^{-11} dpa/s is 600 K which means that the 575 K sample would not be relaxed. It

therefore appears that irradiation aids in the relaxation process. If
we assume that the relaxation time under irradiation at 575 K is about
10 days and would be 171 s at 729 K where Weber measured it, Q = 1.93
and $t_o = 1.04 \times 10^{11}$ s. This change makes it possible to predict
relaxation at 575 K; but, as is shown in Fig. 5 the predicted relaxation
temperatures will not vary greatly over a wide range of dose rate. In
Fig. 5 the effect of dose rate on final damage state is shown for damage
rates varying from 10^{18} dpa/s for natural minerals to about 10^{-3} dpa/s
for ion implantation. The range from about 10^{-14} to 10^{-18} dpa/s is that
expected for high level nuclear waste[8], depending on the age of the
waste form. It may be seen that the two choices for the relaxation
properties make only a small difference; materials stored and irradiated
below about 425 K will not be relaxed while those stored and irradiated
below about 650 K will be amorphous. This is agreement with the natural
zirconolite being amorphous.

IV. Discussion

Development of a model to explain the temperature- and damage
rate-dependence of swelling for plutonium-substituted zirconolite has
not been easy. Many earlier models have been tried and discarded for
one reason or another. One important effort (unpublished) involved an
attempt to explain the measured results at 575 K by invoking continuous
recrystallization of the damaged regions. The assumption that the
recrystallization rate was proportional to the contact area between the
crystalline remanents and the amorphous tracks provided a
continuously-decreasing recovery rate as the material became amorphous.
This model failed because (1) the rate at which the material became

amorphous was slower than the model presented here, and (2) the temperature range over which important changes could be observed was very narrow even for unrealistically small activation energies (e.g. 0.25 eV). Even then the effects observed at 575 K would not have been seen at temperatures as close as 570 K or 580 K, a result we felt not in accord with expected behavior.

The simpler model presented here overcomes many previous objections and explains many of the observations. Further it makes possible predictions concerning temperature and dose rate regimes not yet studied experimentally. The model also suggests that amorphization occurs by two different processes which depend on temperature and which probably also depend on dose rate. At low temperatures, 350 K for this material, damage tracks appear to be amorphous regions with much lower density than that for the crystalline material and also lower than that for the terminal amorphous material. Our assumption of a second overlapping damage track causing relaxation to the final state (another lower energy metamict phase), very nearly fits the observed swelling curve for the low-temperature irradiation.

The parameters required to approximate the 575 K result indicate that the initial damage region at 575 K has a much higher density that that at 350 K, while still dilated by comparison with the starting material. In our model a second damage event again results in the terminal phase, but the situation is different from the lower-temperature case in that the terminal density is reduced by redamage. Here the model proposed by Pedraza and Mansur [13,14], involving accumulation of a critical concentration of defects leading to

conversion to a lower-energy amorphous condition, may be applicable; the unifying theme in their work and ours is that conversion in accompanied by dilation.

The difference between the density of the terminal phases at 350 K and 575 K makes it possible to explain another interesting observation[3]. After irradiation at 575 K for 430 days a sample was cooled to 350 K and irradiation was continued. The material almost immediately swelled to the same value that was observed for a continuous irradiation at 350 K. The rapid expansion is explained by cur model if each damage event transformed a large quantity of amorphous material. The reverse experiment (heating from 350 K to 575 K) was not performed, but our model would predict a rapid transformation back to the swelling value found at 575 K.

One of the most significant observations in the earlier work is that repeated damage of this material results in a halving of stored energy [4]. Subsequent calculations have demonstrated that this effect is the result of reordering of atoms within the metamict state rather that reduction of internal strains [15]. Stored energy results for the high-dose regime (in which an inverse relationship was noted between stored energy and damage level) are tabulated in Table 1, along with corresponding data from Fig. 2 on damage fractions.

Comparison of the results for 224 days and 558 days, the interval during which the greatest reduction of stored energy occurred, is most useful. Here it is apparent that the increase in energy that accompanies conversion of the 10% undamaged material is far outweighed

by the effects of redamage. It is not possible to determine from direct measurement the stored energy value characteristic of once-damaged material, due to the presence of multiple damage states at those doses where the fraction of singly-damaged material is large. However, if it is assumed that redamaged material has a constant value of 51 J/g (as was the case at 1198 days) then the stored energy values of Table 1 can only be accounted for by taking the energy for once-damaged material to be very high, on the order of 200 kJ/kg. This large difference in stored energy between once-damaged and multiply-damaged material indicates the importance of assessing as precisely as possible the extent of redamage in materials converted to the amorphous condition by irradiation. It should also be pointed out that the large difference was observed for material damaged at 350 K where the initial damage state has a much lower density It would be interesting to have the same information about the material damaged at 575 K.

The damage rate calcu.ations (Fig. 5) allow predictions of technological importance to be made. First, unless nuclear waste is stored at temperatures greater than 723 K, the material studied here, a major phase of the SYNROC ceramic waste form, will become amorphous. However, if amorphization is accompanied by unacceptable degradation of properties, storage facilities could be designed to maintain temperatures greater than this value and the crystalline state could be preserved. The analysis also suggests that the amorphous state could be different depending on the temperature, with a less dense phase present for temperatures below 473 K. The fracture and leaching behavior of these two materials might be different, again suggesting the possible desirability of temperature control.

The observed differences between amorphous phases formed at different temperatures and doses might have significance beyond the field of nuclear waste, for example in the area of ion implantation. This technique is gaining importance as a way to improve the properties of both metals and ceramics, by creating a doped amorphous layer that increases resistance to wear or corrosion. With respect to wear, the present findings suggest that lower implantation levels with their accompanying higher surface compression, may give best mechanical properties. On the other hand, corrosion resistance could be enhanced by heavy doses designed to reduce stored energy of the implanted layer.

VI. Conclusions

Amorphization by self-irradiation of $CaPuTi_2O_7$ is temperature and dose dependent. Experimental evidence suggests the existence of two or more amorphous phases which transform to other amorphous phases under irradiation. Application of a simple model suggests two distict mechanisms for the formation of the terminal amorphous phases at high damage. At 350 K the initial amorphous phase has a lower density than the terminal phase while at 575 K the opposite is true. At the higher temperature the initial damage regions are larger and have a density between the crystalline and terminal phases. The phase present at high doses is less dense at 350 K than at 575 K but transforms rapidly when the temperature is lowered; the model predicts the reverse transformation if the temperature is raised. Combined experiment and modelling can be used to predict behavior over a wide range of damage rates from those characteristic of natural minerals to those typical of

ion implantation.

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University of Connecticut.

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Table 1. Damage level, stored energy, and corresponding damage
fractions for $CaPuTi_nO_7$ self-damaged near 300K.

Damage level, days	Stored energy, kJ/kg	Percent undamaged	Percent damaged once	Percent redamaged
154	100	18	32	50
224	92	10	23	67
558	59	0	2	98
1198	51	0	0	100

FIGURE CAPTIONS

Figure 1: Bulk swelling of [239]Pu-substituted zirconolite as a function of storage time and damage dose. Ambient temperature is estimated to be 350 K. [from Ref. 3.]

Figure 2: Calculated fraction of undamaged, damaged once, damaged one or more times, or damaged two or more times versus storage time and damage dose.

Figure 3: Swelling versus damage events per cascade volume (which is proportional to damage dose) calculated for density ratios $r_a = 0.95$ and r_i as indicated.

Figure 4: Calculated swelling curves designed to simulate the swelling resulting from self-irradiation of [239]Pu-substituted zirconolite.

Figure 5: Calculated (a) recrystallization and (b) and (c) relaxation temperatures for the relaxation of the structure of the terminal amorphous phases. versus the irradiation dose rate. Curve (b) is based on the DTA results of Weber[6] while curve (c) incorporates irradiation-assisted transformations to the final conditions.
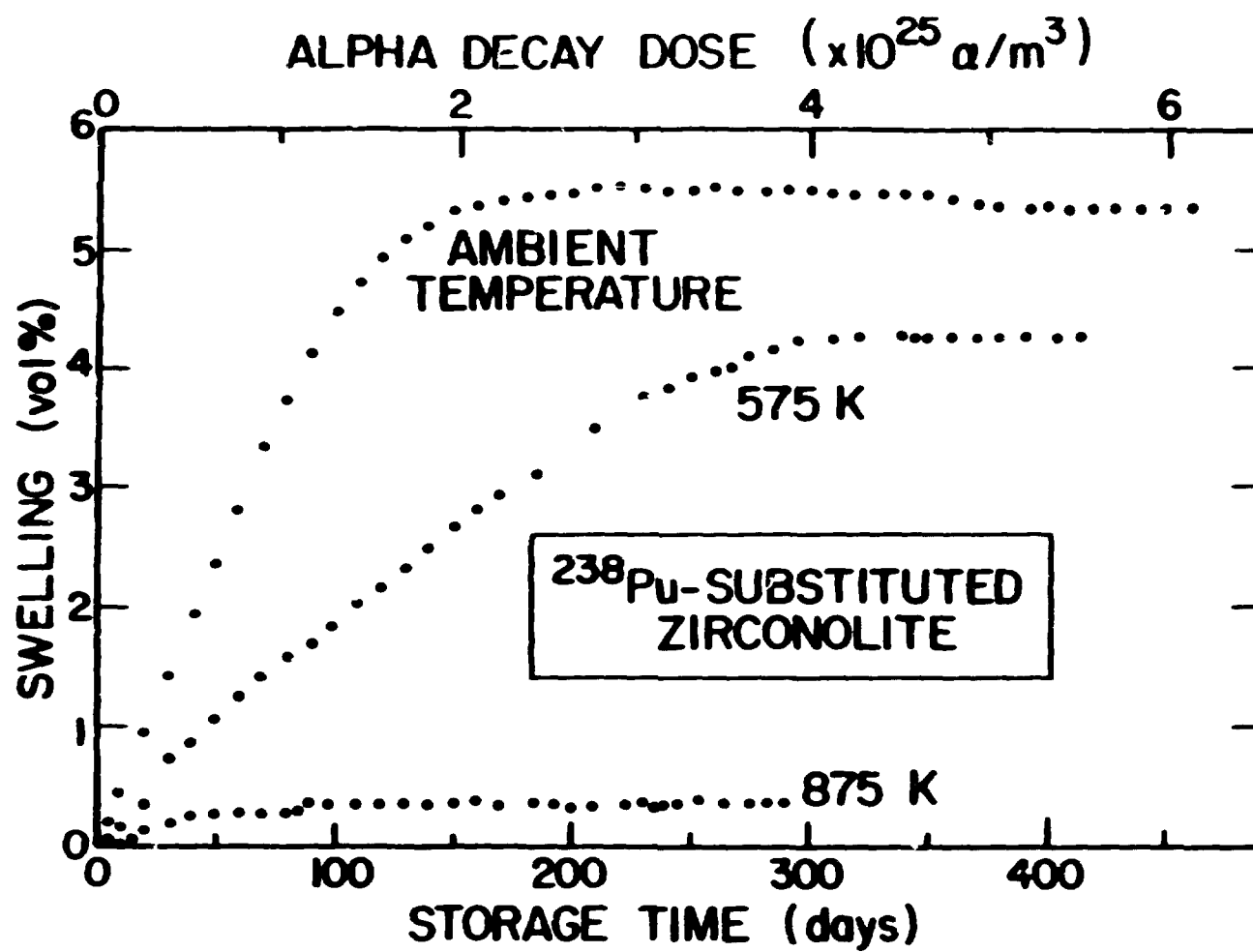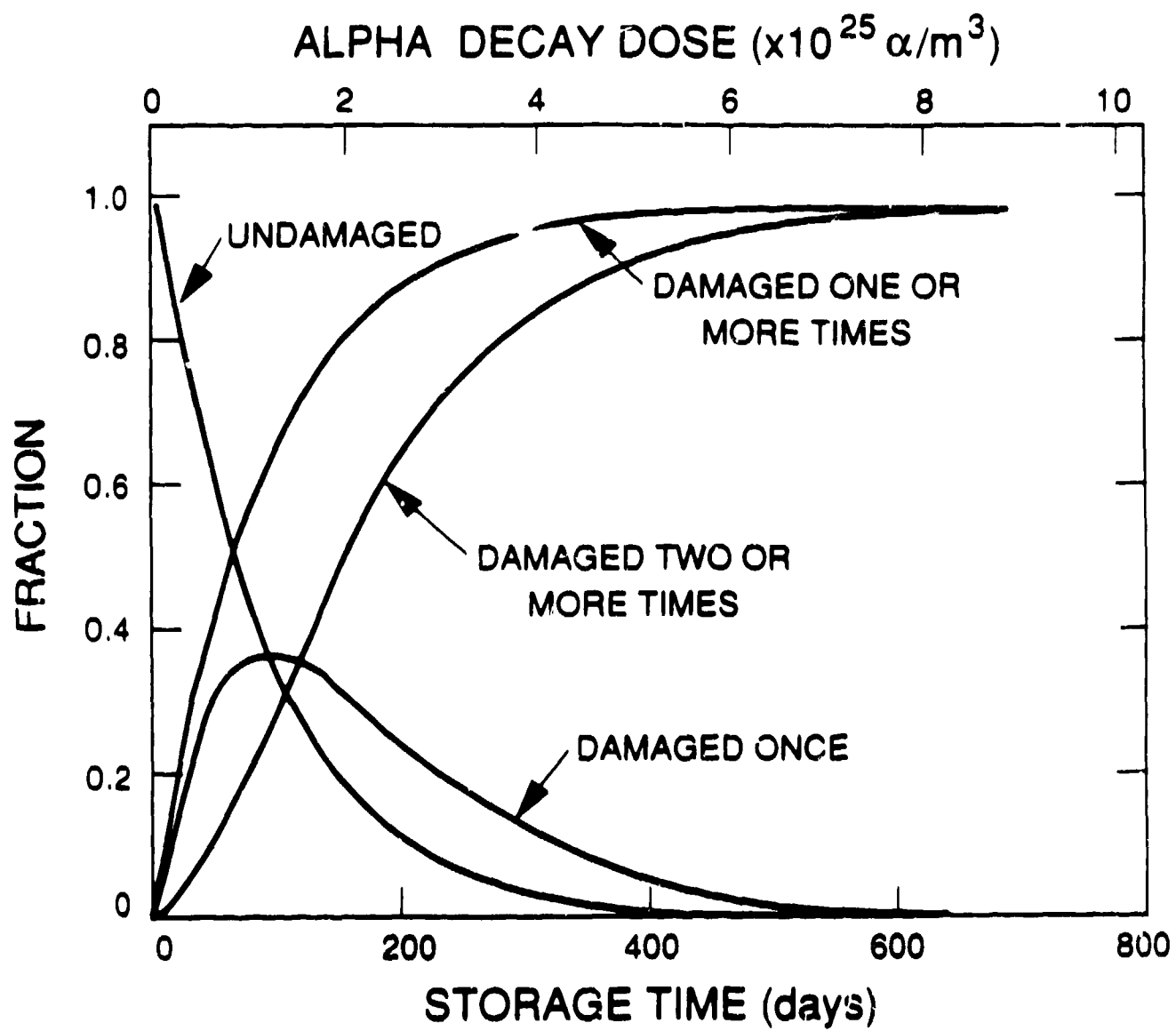
FIGURE 1

ALPHA DECAY DOSE ($\times 10^{25}\,\alpha/m^3$)

FRACTION vs STORAGE TIME (days)

UNDAMAGED

DAMAGED ONE OR MORE TIMES
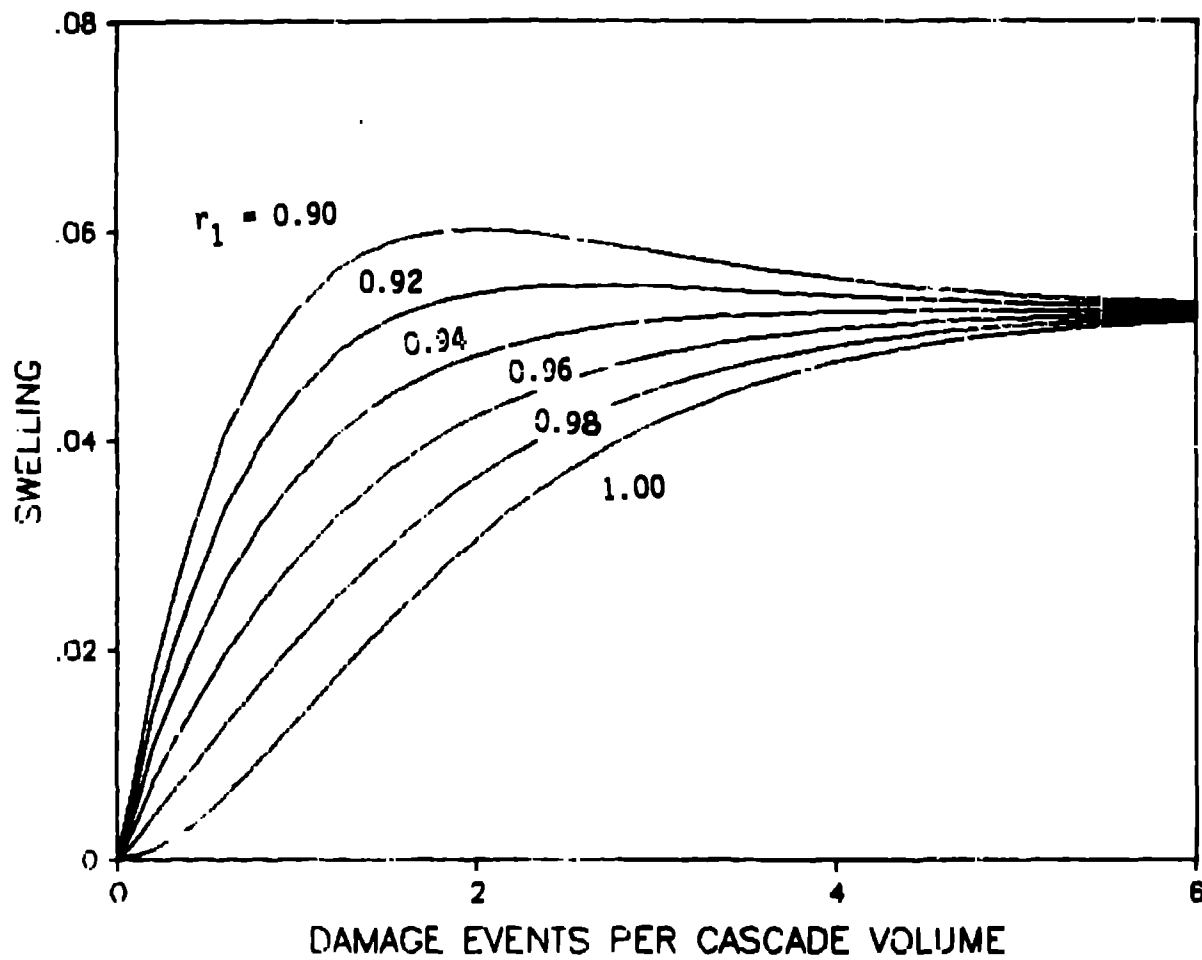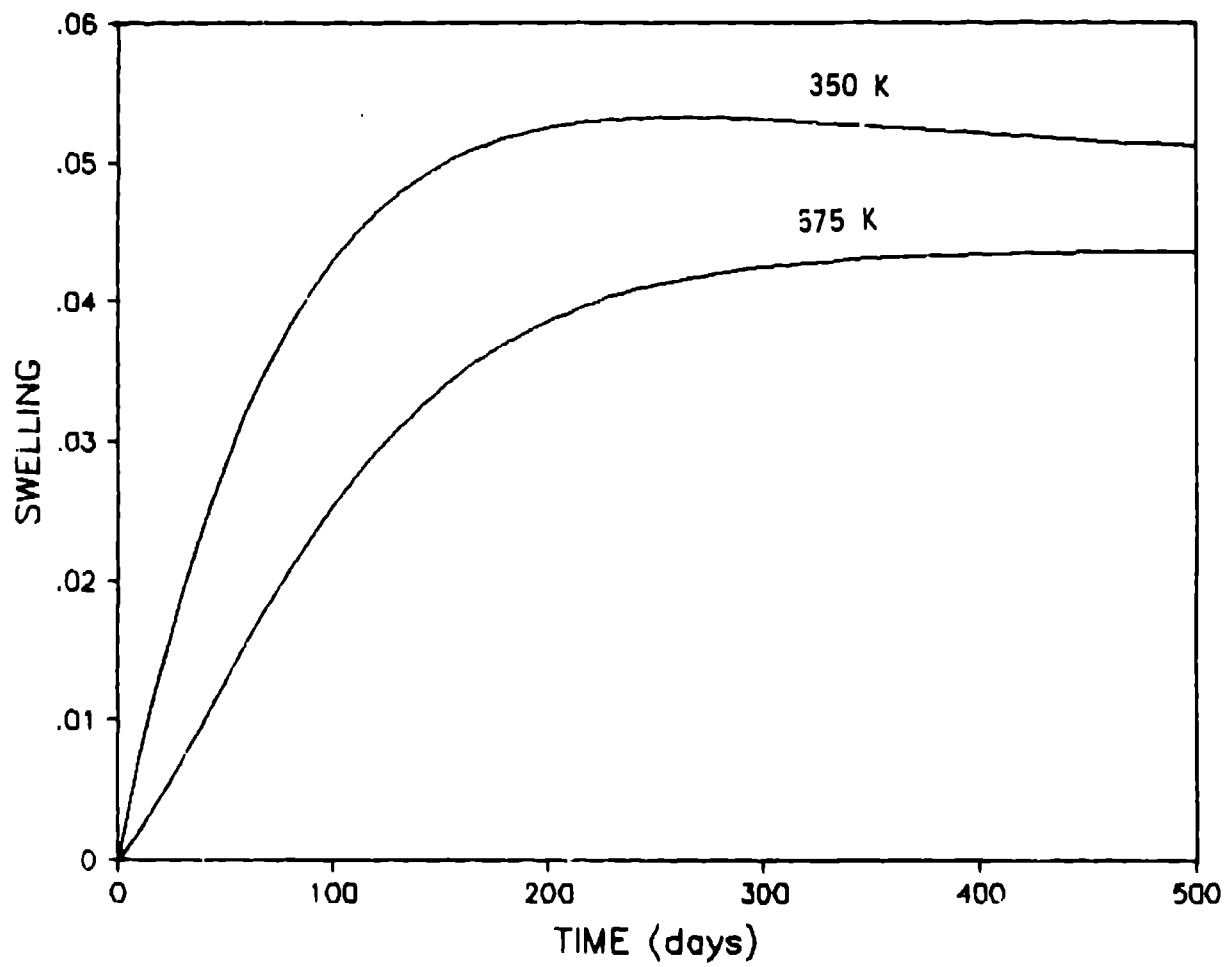
DAMAGED TWO OR MORE TIMES

DAMAGED ONCE

FIGURE 2

DAMAGE EVENTS PER CASCADE VOLUME

FIGURE 3

FIGURE 4

FIGURE 5